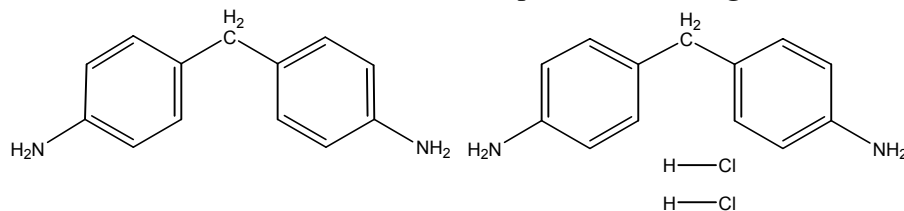


## 4,4'-METHYLENEDIANILINE AND ITS DIHYDROCHLORIDE

CAS Nos. 101-77-9 and 13552-44-8

First Listed in the *Fourth Annual Report on Carcinogens*



4,4'-Methylenedianiline

4,4'-Methylenedianiline dihydrochloride

### CARCINOGENICITY

4,4'-Methylenedianiline and its dihydrochloride are *reasonably anticipated to be a human carcinogen* based on sufficient evidence of carcinogenicity in experimental animals (NTP 248, 1983; IARC V.39, 1986; IARC S.7, 1987). When administered in the drinking water, 4,4'-methylenedianiline dihydrochloride increased the incidences of thyroid follicular cell carcinomas and neoplastic nodules of the liver in male rats; follicular cell and C-cell adenomas of the thyroid gland in female rats; thyroid follicular cell adenomas and hepatocellular carcinomas in mice of both sexes, adrenal pheochromocytomas in male mice; and hepatocellular adenomas and malignant lymphomas in female mice (NTP 248, 1983). In a study in rats in which 4,4'-methylenedianiline was administered orally in conjunction with a known carcinogen, the incidence of thyroid tumors was greater than that produced by the carcinogen alone (IARC V.39, 1986).

There are no data available to evaluate the carcinogenicity of 4,4'-methylenedianiline and its dihydrochloride in humans (IARC V.39, 1986; IARC S.7, 1987).

### PROPERTIES

4,4'-Methylenedianiline is a light brown crystalline solid with a faint amine-like odor. It is very slightly soluble in water and very soluble in acetone, alcohol, benzene, and ether. It is combustible when exposed to heat or flame. When heated to decomposition, it emits toxic fumes of aniline and nitrogen oxides (NO<sub>x</sub>). It is estimated that the 4,4'-methylenedianiline produced domestically is 40%-70% pure, while the imported product is approximately 98% pure. The dihydrochloride is a crystalline solid that is soluble in water. No other data were available.

### USE

Approximately 98% of the 4,4'-methylenedianiline produced domestically is used as a chemical intermediate in the closed-system production of isocyanates and polyisocyanates. These are used extensively in the manufacture of rigid polyurethane foams for insulation and semiflexible polyurethane foams for automobile safety cushioning (OSHA FR, 1987). 4,4'-Methylenedianiline is also used in the production of wire coatings, in the determination of tungsten and sulfates, as an analytical reagent, a corrosion inhibitor, and a monomer for

polyamide and polyimide resins. No data were available on the use of the dihydrochloride other than its use as a research chemical (IARC V.39, 1986).

## PRODUCTION

Chem Sources identified fourteen distributors of 4,4'-methylenedianiline in 1990 (Chem Sources, 1991). No production data or information on the dihydrochloride were available. The USITC identified two U.S. producers of 4,4'-methylenedianiline in 1989, but no production figures were reported (USITC, 1990). Approximately 3.4 million lb of 4,4'-methylenedianiline were imported into the U.S. in 1989 (USDOC Imports, 1990). OSHA reported that 4,4'-methylenedianiline is manufactured by six companies at seven locations in four states. In 1987, approximately 600 million lb were produced and used captively as a chemical intermediate, 4.5 million lb were produced domestically for sale, and an additional 1 million lb were imported (OSHA FR, 1987). U.S. imports of 4,4'-methylenedianiline totalled more than 1.4 million lb in 1984, and over 933,000 lb in 1983 (USDOC Imports, 1985; USITCa, 1984). Production of 4,4'-methylenedianiline in 1983 was estimated to be approximately 198 to 396 million lb/yr by a total of seven manufacturers (Chem. Week, 1984a). The USITC identified four companies that produced an undisclosed volume of 4,4'-methylenedianiline in 1983 (USITC, 1984). The 1979 TSCA Inventory reported that nine U.S. companies produced over 30 million lb of 4,4'-methylenedianiline in 1977 and two companies imported 110,000 lb of the chemical into the United States. The CBI Aggregate was between 100 million and 1 billion lb. EPA also reported one producer and one importer of 4,4'-methylenedianiline dihydrochloride in 1977, but no volumes were given (TSCA, 1979). 4,4'-Methylenedianiline has been produced commercially in the United States since the early 1920s (IARC V.39, 1986).

## EXPOSURE

The primary routes of potential human exposure to 4,4'-methylenedianiline are inhalation, ingestion, and dermal contact. Potential exposure occurs during production, packaging, and reprocessing of the chemical and during its use in epoxy resins. The National Occupational Exposure Survey (1981-1983) estimated that 2,279 total workers including 1,170 women, potentially were exposed to the compound in the workplace (NIOSH, 1984). The National Occupational Hazard Survey, conducted by NIOSH from 1972 to 1974, estimated that 9,163 workers were potentially exposed to 4,4'-methylenedianiline in the workplace in 1970 (NIOSH, 1976). The ACGIH considers 4,4'-methylenedianiline a suspected human carcinogen, notes the potential for skin absorption and recommends a threshold limit value time-weighted average (TLV-TWA) of 0.1 ppm (0.8 mg/m<sup>3</sup>) (ACGIH, 1986). The Methylenedianiline Mediated Rulemaking Advisory Committee convened by OSHA published an industry and exposure profile in 1987. The industry sectors were divided into three categories: production for 4,4'-methylenedianiline diisocyanate synthesis or sale, reprocessing, and use in epoxies. In the production sector, the committee estimated a reasonable worst-case of 525 workers were potentially exposed to 1-41 ppb of this chemical. In the reprocessing sector, the Committee estimated 756 workers were potentially exposed to 1-20 ppb with a maximum of 250 ppb. At least 3,500 workers were exposed in the epoxy use sector with average exposures varying from 0.1 to 20 ppb. In addition, an estimated 252 maintenance workers were exposed at levels up to 250 ppb. FDA reports that levels of 4,4'-methylenedianiline in food, food additives, or food packaging are so low that the potential daily intake is virtually nil. Potential consumer exposure may occur through dermal contact with trace amounts found in automobile cushioning or epoxy containing products. It rapidly degrades in vapor (half-life = 1.6 hours). In water it covalently

binds to humic material, with significant photooxidation in water (half-life of photooxidants ~ 19-30 sunlight hours).

The primary route of potential exposure to 4,4'-methylenedianiline dihydrochloride is dermal contact. This potential exposure could occur during its production or during the use of the chemical by laboratory personnel. Data on the number of people potentially exposed were not available.

## **REGULATIONS**

EPA regulates 4,4'-methylenedianiline under the Clean Air Act (CAA), Superfund Amendments and Reauthorization Act (SARA), and Toxic Substances Control Act (TSCA). 4,4'-Methylenedianiline is subject to reporting requirements under CAA, SARA, and TSCA. Testing rules have been promulgated under CAA and TSCA. FDA regulates 4,4'-methylenedianiline under the Food, Drug, and Cosmetic Act (FD&CA) as a food additive. OSHA has been going through a rulemaking process to determine a standard for occupational exposure to this chemical. There was no information available concerning the regulation of the dihydrochloride. OSHA regulates 4,4'-methylenedianiline and its dihydrochloride under the Hazard Communication Standard and as chemical hazards in laboratories. Regulations are summarized in Volume II, Table B-82.